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# DHS Internship Summary-Crystal Assembly at Different Length Scales

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## **DHS Internship Summary**

Lidiya Mishchenko / DHS 2008 Fellow

**Brief project Description:**

## Crystal Assembly at Different Length Scales

I was part of a project in which in situ atomic force microscopy (AFM) was used to monitor growth and dissolution of atomic and colloidal crystals. At both length scales, the chemical environment of the system greatly altered crystal growth and dissolution. Calcium phosphate was used as a model system for atomic crystals. A dissolution-reprecipitation reaction was observed in this first system, involving the conversion of brushite (DCPD) to octacalcium phosphate (OCP). In the second system, polymeric colloidal crystals were dissolved in an ionic solvent, revealing the underlying structure of the crystal. The dissolved crystal was then regrown through an evaporative step method. Recently, we have also found that colloids can be reversibly deposited in situ onto an ITO (indium tin oxide) substrate via an electrochemistry setup. The overall goal of this project was to develop an understanding of the mechanisms that control crystallization and order, so that these might be controlled during material synthesis.

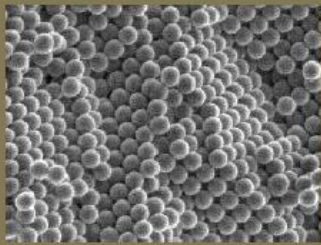
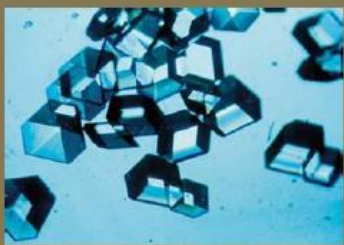
**Details of the project:**

Controlled assembly of materials over a range of length scales from molecules to nanoparticles to colloids is critical for designing new materials. In particular, developing materials for sensor applications with tailorable properties and long range order is important. In this work, we examine two of these length scales: small molecule crystallization of calcium phosphate (whose crystal phases include DCPD, OCP, and HAP) and colloidal crystallization of Poly(methyl methacrylate) beads. Atomic Force Microscopy is ideal for this line of work because it allows for the possibility of observing non-conducting samples in fluid during growth with high resolution ( $\sim 10$  nm). In fact, during atomic crystal growth one can observe changes in

atomic steps, and with colloidal crystals, one can monitor the individual building blocks of the crystal.

Colloids and atoms crystallize under the influence of different forces acting at different length scales as seen in **Table 1**. In particular, molecular crystals, which are typically dominated by ionic and covalent bonding, are an order of magnitude more strongly bonded than colloidal crystals. In molecular crystals, ordering is driven by the interaction potentials between molecules. By contrast, colloidal assembly is a competition between the repulsive electrostatic forces that prevent aggregation in solution (due to surface charge), and short-range van der Waals and entropic forces that leads to ordering.

**Table 1. The different growth units and forces involved in colloidal and atomic crystallization**

Colloidal Crystal	Atomic or Molecular Crystal
	
<small><a href="http://people.umass.edu/dinsmore/Phys850/poster_2_exp.jp">http://people.umass.edu/dinsmore/Phys850/poster_2_exp.jp</a></small>	<small><a href="http://en.wikipedia.org/wiki/File:Insulincrystals.jpg">http://en.wikipedia.org/wiki/File:Insulincrystals.jpg</a></small>
<b>Growth unit:</b> Colloid ( $10^{-9} - 10^{-6}$ m)	<b>Growth unit:</b> ion/molecule ( $10^{-10}$ - $10^{-9}$ m)
<b>Forces<sup>2</sup>:</b> (in solution) Van der Waals: 0.4 – 4 kJ/mol Electrostatic: 20 kJ/mol Depletion: 73 kJ/mol <sup>1</sup> (for 300K) Entropic: 2.5 kJ/mol	<b>Forces<sup>2</sup>:</b> Van der Waals: 0.4 – 4 kJ/mol Electrostatic: 20 kJ/mol Hydrogen bonding: 12-30 kJ/mol Ionic and covalent: 100-800 kJ/mol

<sup>1</sup>Savage, et al. *PRL* 102, 198302 (2009)

<sup>2</sup><http://web.virginia.edu/Heidi/chapter1/chp1frameset.htm>

Understanding atomic crystallization is fundamentally important for fabrication of tailorable crystalline materials, for example for biological or chemical sensors. The

transformation of brushite to OCP not only serves as a model system for atomic crystal growth (applicable to many other crystal growth processes), but is also important in bone cements.

Colloidal crystals have unique optical properties which respond to chemical and mechanical stimuli, making them very important for sensing applications. The mechanism of colloidal crystal assembly is thus fundamentally important. Our in situ dissolution and regrowth experiments are one good method of analyzing how these crystals pack under different conditions and how defect sites are formed and filled. In these experiments, a silica additive was used to strengthen the colloidal crystal during initial assembly (ex situ) and to increase domain size and long range order.

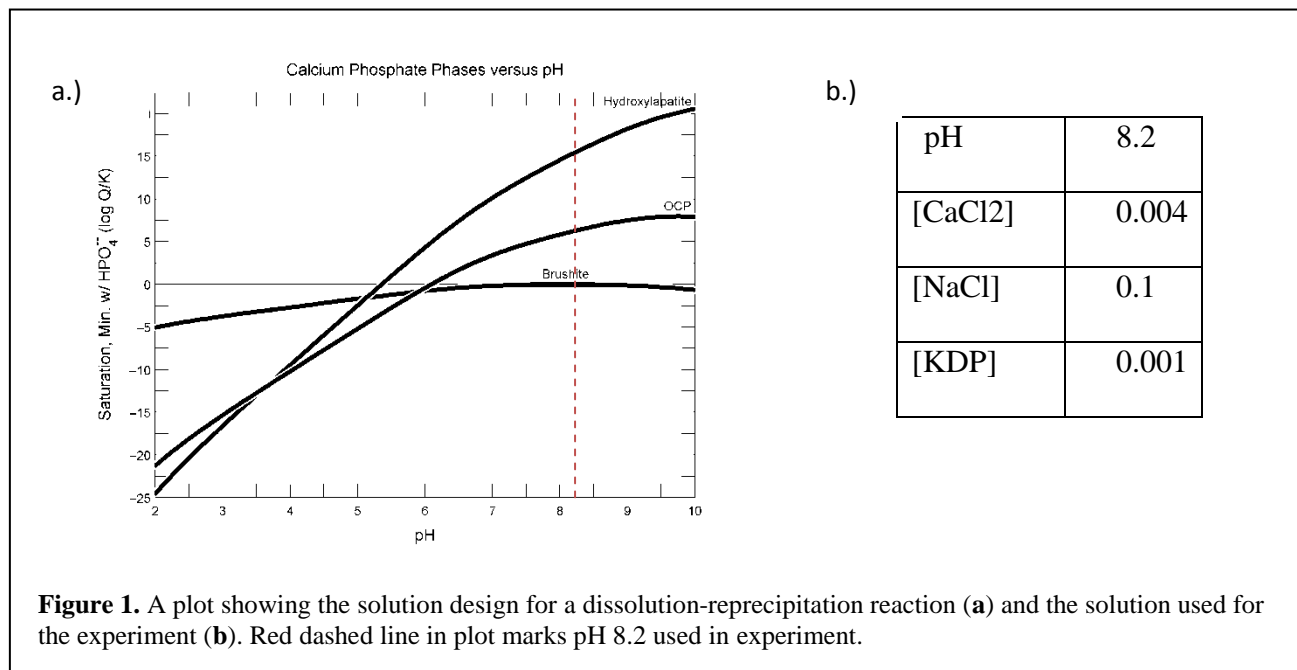
Reversible electrodeposition of colloids onto a conductive substrate (ITO in our case) is another system which can further our knowledge of colloidal assembly. This experiment holds promise of allowing in situ observation of colloidal crystal growth and the influence of certain additives on crystal order. The ultimate goal would be to achieve long range order in these crystals by changing the surface charge or the growth environment.

Methods:

Calcium Phosphate Dissolution and Reprecipitation:

A solution (see **Figure 1b**) supersaturated with respect to octacalcium phosphate and hydroxyapatite and undersaturated with respect to other phases was designed (modeling plot shown in **Figure 1a**) and mixed. Water and then this solution were flowed with a peristaltic pump into an AFM fluid cell containing a cleaved brushite crystal. The surface of the brushite crystal was monitored in situ as dissolution and growth were observed over the course of hours (with the solution refreshed periodically in the cell). The sample was left in solution over the

course of a few days and then removed and air dried. A Raman microscope was used to analyze the new phase on the brushite crystal.



#### Colloidal Crystal Growth/Electrodeposition:

Monodispersed colloidal particles of PMMA (300-400 nm diameter) were synthesized by emulsion polymerization. 0.025 mL of a 9 vol% ‘stock’ aqueous colloidal suspension (cleaned by dialysis) was added to 5 mL of distilled/DI H<sub>2</sub>O, and 0.005 mL of added hydrolyzed TEOS solution. The TEOS solution consisted of 1:1:1.5 ratio by weight of TEOS (Tetraethyl orthosilicate, a precursor to silica/glass), 0.10 M HCl, and EtOH, respectively, stirred at room temperature for 1 h prior to use. Si substrates, cleaned in piranha solution, were vertically suspended in the vial containing the colloid/TEOS suspension. The solvent content was evaporated slowly over a period of 1 day in a 60°C oven, to allow the deposition of a thin film onto the suspended substrate.

Colloidal crystals (evaporatively deposited as described above) were placed in an AFM fluid cell. Water and then a solution containing NaCl ( $\sim 0.2\text{M}$ ) and colloids ( $\sim 0.5\%$  by volume) were flowed with a peristaltic pump into the cell. The surface of the colloidal crystal was monitored in situ as dissolution was observed over the course of hours.

Regrowth was achieved by repeated cycles of flowing in  $\sim 4.5\%$  by volume aqueous colloidal solution and partially drying out the fluid cell with nitrogen gas to increase the concentration of colloids at the surface of the crystal. Water was flowed in after each cycle and the surface was imaged with AFM.

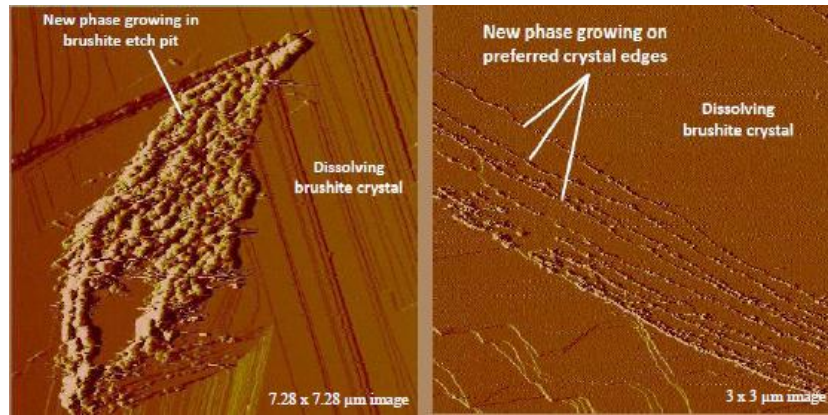
A piranha-cleaned ITO sample was used as a working electrode in a 3 electrode electrochemical setup in an AFM fluid cell. A silver wire was used as a reference electrode and a platinum wire was used as a counter electrode. An aqueous solution of approximately  $0.1\text{ M}$  NaCl and  $0.5\%$  by volume of PMMA colloids was flowed into the fluid cell containing the substrate. The voltage between the working electrode and the silver wire was varied as deposition and desorption were observed. (A current was driven between the working and counter electrode to force the voltage between the working electrode and the reference electrode to maintain certain values.)

## Results and Discussion:

### Calcium Phosphate Dissolution and Reprecipitation:

A dissolution-reprecipitation reaction, involving conversion of brushite (DCPD) to octacalcium phosphate (OCP), was observed in situ.



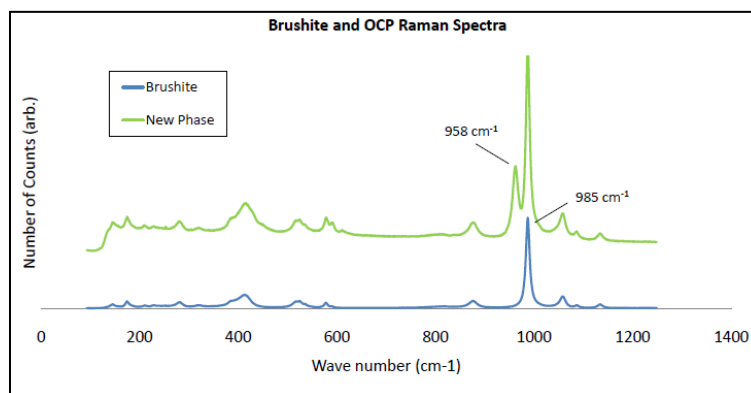


**Figure 2.** AFM in situ images showing a new OCP phase growing in a brushite etch pit (left) and on specific brushite crystal planes (right).

As seen in the in situ AFM images above, the brushite crystal (DCPD) dissolved because it was undersaturated at the pH of the solution. Both OCP and HAP were supersaturated, but OCP is kinetically favored and was thus the observed phase.

Raman microscopy revealed a new strong peak (at  $958\text{ cm}^{-1}$ ) in the crystal spectrum which can be attributed to an OCP phase (on the surface of the brushite).

	OCP	DCPD (Brushite)
P-O stretching mode ( $\nu_1$ ) of the $\text{PO}_4$ group	$958\text{ cm}^{-1}$	$985\text{ cm}^{-1}$

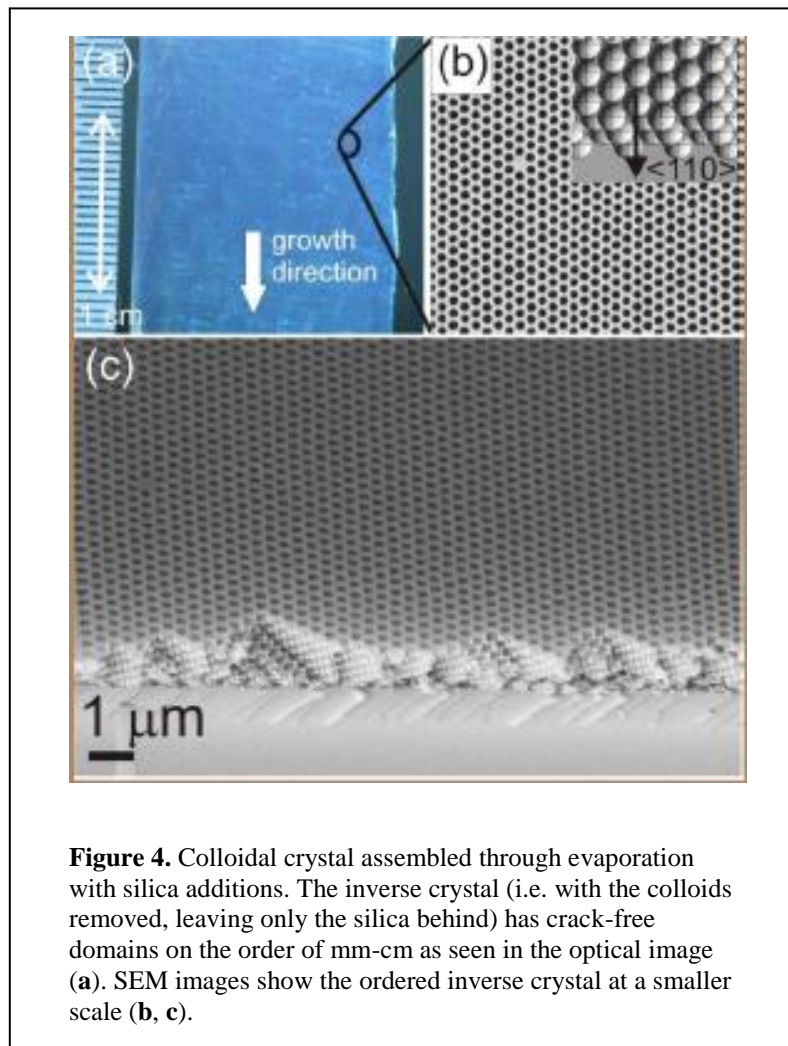


<sup>1</sup>Koutsopoulos, S. *Wiley Periodicals*. "Synthesis and characterization of hydroxyapatite crystals: A review study on the analytical methods." (2002)

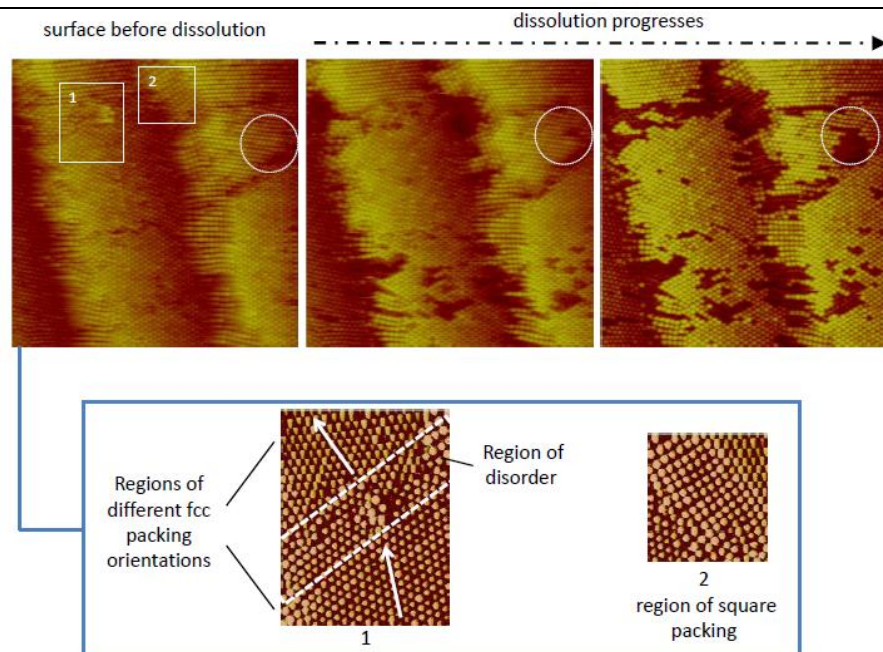
**Figure 3.** Raman microscopy data plot showing the spectrum of the original brushite substrate (blue line) and the spectrum of the sample after a dissolution-precipitation reaction (green). The table above indicates the significance of the main peaks seen in the plot. Note: spectra vertically shifted for clarity.

## Colloidal Crystal Growth:

Colloidal crystals were prepared by evaporative deposition from a suspension of colloids and silica (TEOS) additions. The silica additions seemed to strengthen the crystal (this crystal did not dissolve as quickly in aqueous solution as ones without additions) and increase long range order. Previous studies (involving Benjamin Hatton and Joanna Aizenberg in Harvard University) reveal that with optimal silica additions, it is possible to remove the colloids and obtain an ordered inverse opal with domain sizes of mm-cm length scales.



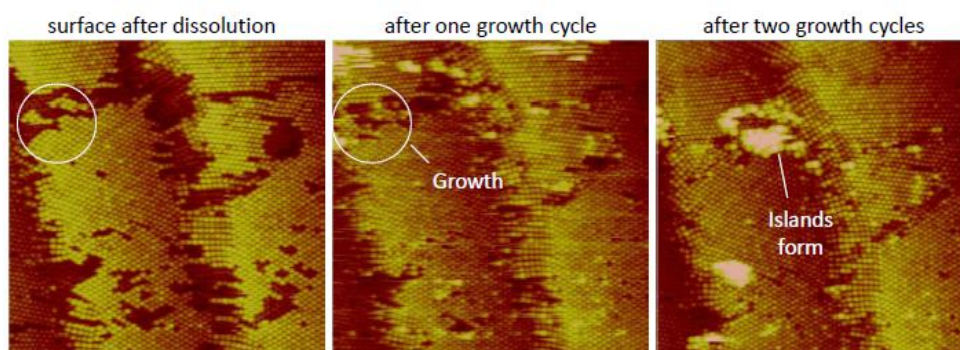
For the first experiment, colloidal crystal dissolution was induced and observed in situ (Figure 5).



**Figure 5.** Sequential AFM images (20 x 20  $\mu\text{m}$ ) shown of the colloidal dissolution process. Circles highlight one region of dissolution. A disordered grain boundary between two different FCC domains and a square packing domain are shown in the inset. Note that these regions dissolve faster than others. Darker colors in larger images indicate lower heights than regions of brighter colors.

The colloidal crystal most likely dissolved due to the presence of ions from the salt solution, though the influence of the scanning AFM tip and the capillary forces induced in the cell during periodic draining and refilling most likely contributed as well.

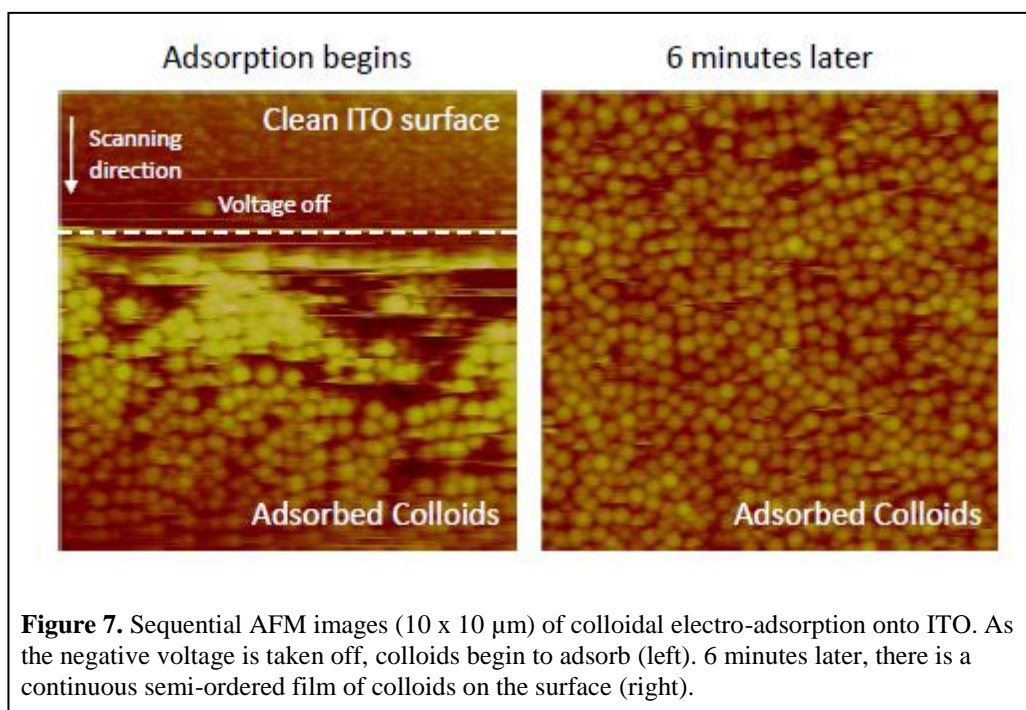
After dissolution was observed for some time, a series of regrowth cycles was performed on the same substrate (**Figure 6**).



**Figure 6.** Sequential AFM images (20 x 20  $\mu\text{m}$ ) shown of the colloidal regrowth process. Circles highlight one region of growth. After two cycles, islands begin to form on the surface of the crystal.

For regrowth, a high concentration (~ 56%) of colloids was necessary for crystallization to take place and we were not able to image this process in situ but only step by step.

Another method of forcing colloids to interact with the surface is through the use of surface charge and electric fields. For the electrochemistry experiment, we observed adsorption onto the ITO substrate without any applied voltage. Since our colloids possess a negative surface charge, it is possible that the ITO substrate has a positive surface charge in our solution. Setting the working electrode voltage to be -500 mV with respect to the silver wire, we were able to remove all of the colloids from the ITO surface. However, as the applied voltage was taken off, the colloids began to readsorb onto the surface as before (**Figure 7**).



Conclusions:

The brushite to OCP conversion revealed that the growth of an HAP phase from solution is a multi-stage process due to the initial growth of other kinetically favored phases such as OCP.

Thus, so far we have only imaged the first stage of this transformation process. Monitoring this multi phase transformation is of importance for bone material applications. Kinetics and phase transitions are also something that must be considered with any crystal growth method.

The dissolution of the colloidal crystal revealed that there might be parts of a crystal that are more vulnerable than others. Disordered parts of the crystal (i.e. grain boundaries), parts of the crystal already containing vacancies, and areas of anomalous packing (i.e. square packing) are more vulnerable to dissolution. This underscores the need to have long range order to prevent degradation of colloidal sensors. The use of silicate additions may be a step towards increasing order and strengthening the crystal mechanically.

The regrowth process allowed us to see approximately how a crystal may go about filling in vacancies during growth. Some vacancies were more difficult to fill in than others, which may help explain the origin of defect sites typically observed in colloidal crystals.

Our work on electrochemical deposition, though preliminary, holds great promise. We are still exploring the possibilities of how we can achieve colloidal crystallinity in our system (changing the surface charge of the substrate, adding chemical substances to the system to modify surface and particle interactions, etc.), but this proof of principle gives us hope that this may be possible. If we can achieve a reversible colloidal crystallization system, there may be many aspects of colloidal assembly that could be explored such as how defects form in crystals, how a crystal may repair these defects, and how chemical surroundings influence long range order.

**My role in this project:**



Christine Orme and I designed the experiments together. She helped me set up and run some of the experiments. I learned how to do most things independently, however. I designed and mixed the solutions for the calcium phosphate experiments. I learned how to run both fluid and dry cell AFMs and how to operate the Raman microscope for sample analysis. I synthesized the colloids we used in the colloidal experiments. I prepared colloidal crystals through evaporative deposition. Recently, Christine Orme and I both ran the electrodeposition experiment side by side.

### **My achievements:**

Many of the results of my experiment may contribute to future publications involving crystal phase transitions and colloidal crystallization. I presented a poster on evaporative colloidal growth involving silica additions at the Thin Film and Crystal Growth Gordon Conference in July. I also put together and presented a poster at the LLNL student symposium which described our results and their possible applications.

One the goals of this project was to further understanding of crystal growth and crystal phases. As already emphasized, atomic crystallization is fundamentally important for fabrication of tailorable crystalline materials, for example for biological or chemical sensors. My work helped with this goal by demonstrating a crystal phase transition in our model calcium phosphate system.

To realize the full potential of colloidal crystals as sensors, it is important to be able to grow large, defect-free crystals. Thus, another one of the goals of this project was to explore colloidal crystal growth and defect formation. My work and preliminary results form a solid basis for achieving this goal by looking at dissolution and regrowth of colloidal crystals as well

as colloidal adsorption onto surfaces. Once we are able to gain more control of our experimental system, it will be possible to explore related aspects of this projects including reducing defect formation and establishing long range order.

### **Impact of internship:**

This internship introduced me to the national laboratory environment. I now know what it would be like to work in a national lab and what possible projects may interest me in Lawrence Livermore National Labs. LLNL hosted weekly seminars for DHS and other summer interns. This was a good networking tool for students and also introduced everyone to the cutting edge research currently being done at the lab. Chris Bailey's talk entitled "The Viral Discovery Platform" and Brooke Buddemeier's talks on nuclear disaster responses were especially fascinating. They explored how basic scientific principles can be very relevant in addressing this nation's top security issues.

My project also had a large impact on my career and academic goals. Working in Christine Orme's lab has greatly expanded my field of knowledge in Atomic Force Microscopy and crystal growth. I fully plan to incorporate these skills into my thesis work.

### **Ideas on relevant areas of research for the DHS mission:**

Atomic and colloidal crystals are areas of research that could help DHS accomplish its mission and goals. These materials are important for developing chemical sensors for detecting and characterizing chemical threats. Crystalline materials are regularly used in sensor applications and there is a need to further our knowledge of their growth and subsequent properties. Synthesis of materials with high purity, correct phase and stoichiometry, long range

order, and low defect density has historically been the rate limiting step in many sensor systems. Right now, this is particularly true of gamma ray detectors needed for homeland security. It is widely appreciated that greater efforts in developing crystallization techniques are needed to create these materials.

Colloidal crystals are important because they are able to change their optical properties in response to chemical surroundings. Because colloidal crystals can also respond to mechanical stimuli, they could also be used to aid in response to explosives by determining the amount of mechanical damage caused by an explosion.

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